

2771-696

Amendments to the Claims:

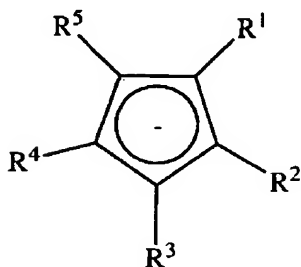
This listing of claims, with claims 65, 108 and 109 amended as set forth below, replaces all prior versions, and listing, of claims in the application.

Listing of Claims:

1. (Previously Presented) A method for depositing a ruthenium thin film onto a substrate, said method comprising:
 - (a) depositing a nucleation layer comprising ruthenium metal onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited using a first ruthenium precursor/co-reactant gas mixture having greater than about 30 mole percent of the co-reactant gas, under nucleation layer CVD conditions including a temperature of from about 250°C to about 340°C and a ruthenium precursor gas flow rate that is sufficient to maintain a surface reaction rate-limited deposition; and
 - (b) depositing an upper layer comprising ruthenium metal onto the nucleation layer by chemical vapor deposition, wherein the upper layer is deposited using a second ruthenium precursor/co-reactant gas mixture having less than 50 mole percent of the co-reactant gas under upper layer CVD conditions, including a ruthenium precursor gas flow rate that is less than that needed to maintain a surface reaction rate-limited deposition.
2. (Previously Presented) The method of claim 1, wherein the upper layer CVD conditions are more reducing than the nucleation layer CVD conditions.
3. (Previously Presented) The method of claim 1, wherein the ruthenium precursor gas flow rate for the nucleation layer is in a range of from about 2 µmol/min to about 100 µmol/min.
4. (Original) The method of claim 1, wherein the nucleation layer CVD conditions comprise pressure in a range of about 0.1 Torr and about 8 Torr.
5. (Previously Presented) The method of claim 1, wherein the nucleation layer CVD conditions comprise pressure in a range of about 0.4 Torr to about 1.6 Torr.
6. (Previously Presented) The method of claim 1, wherein at least one of the first and second ruthenium precursor/co-reactant gas mixtures further comprises an inert gas.
7. (Previously Presented) The method of claim 1, wherein the first and second ruthenium precursors are the same.
8. (Previously Presented) The method of claim 1, wherein the first and second ruthenium precursors are different.

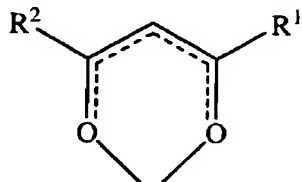
2771-696

9. (Cancelled).
10. (Cancelled)
11. (Previously Presented) The method of claim 1, wherein from about 80 mole% to about 95 mole% of the first ruthenium precursor/co-reactant gas mixture is a co-reactant gas.
12. (Previously Presented) The method of claim 11, wherein the first co-reactant gas comprises oxygen.
13. (Previously Presented) The method of claim 1, wherein the first and the second ruthenium precursors are independently selected from the group consisting of ruthenocenes, ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, ruthenium oxides and ruthenium halides.
14. (Original) The method according to claim 13, wherein the ruthenocenes have the formula $(Cp')Ru(Cp'')$, where Cp' and Cp'' can be same or different and have the general formula:



where $R^1 - R^5$ are independently selected from the group consisting of H, F, and straight-chained or branched $C_1 - C_5$ alkyl groups.

15. (Cancelled)
16. (Original) The method of claim 13, wherein the ruthenocene comprises $Ru(EtCp)_2$ or $Ru(Cp)_2$.
17. (Original) The method according to claim 13, wherein the ruthenium β -diketonates have the formula $Ru(\beta\text{-diketonate})_3$, where β -diketonate has the general formula:



2771-696

where R^1 and R^2 are independently selected from the group consisting of H, F, straight-chained or branched $C_1 - C_5$ alkyl groups, and fluorine-substituted straight-chained or branched $C_1 - C_5$ alkyl groups.

18. (Original) The method of claim 13, wherein the ruthenium β -diketonate comprises a compound selected from the group consisting of: tris(2,4-pentanedionate) ruthenium ($Ru(acac)_3$); tris(1,1,1-trifluoro-2,4-pentanedionate) ruthenium ($Ru(tfac)_3$); tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ruthenium ($Ru(thd)_3$); tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) ruthenium ($Ru(hfac)_3$); tris(2,2,7-tetramethyl-3,5-octanedionate) ruthenium ($Ru(tod)_3$); tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) ruthenium ($Ru(fod)_3$); and tris(2,4-octanedionate) ruthenium ($Ru(od)_3$).
19. (Original) The method of claim 13, wherein the ruthenium β -diketonate comprises $Ru(thd)_3$ or $Ru(hfac)_3$.
20. (Previously Presented) The method of claim 1, wherein the rate of introduction of the first ruthenium precursor is in a range of about $15 \mu\text{mol/min}$ to about $30 \mu\text{mol/min}$.
21. (Previously Presented) The method of claim 1, wherein the substrate comprises a substrate material selected from the group consisting of silicon, silicon dioxide, silicon nitride, hafnium silicon oxide, hafnium silicon oxynitride, Co(WP), copper, titanium nitride, titanium aluminum nitride, tantalum nitride, tantalum pentaoxide, barium strontium titanate and lead zirconate titanate.
22. (Original) The method of claim 1, wherein the resistivity of the nucleation layer is less than about $250 \mu\Omega\text{-cm}$.
23. (Original) The method of claim 1, wherein the rate of deposition of the nucleation layer is in a range of about 5 \AA/min to about 1 \AA/min .
- 24-26. (Cancelled)
27. (Previously Presented) The method of claim 1, wherein the upper layer consists essentially of ruthenium metal.
28. (Original) The method of claim 1, wherein the upper layer CVD conditions comprise temperature in a range of about 280°C and about 400°C .
29. (Original) The method of claim 1, wherein the upper layer CVD conditions comprise pressure in a range of about 0.1 Torr and about 2 Torr.

2771-696

30. (Previously Presented) The method of claim 1, wherein the upper layer CVD conditions comprise pressure in a range of about 0.2 Torr to about 1.0 Torr.
31. (Previously Presented) The method of claim 1, wherein both the first and the second ruthenium precursor/co-reactant gas mixtures further comprise an inert gas.
- 32-36. (Cancelled)
37. (Previously Presented) The method of claim 1, wherein from about 1 mole% to about 10 mole% of the second ruthenium precursor/co-reactant gas mixture is the co-reactant gas.
38. (Previously Presented) The method according to claim 37, wherein the second co-reactant gas comprises oxygen.
39. (Previously Presented) The method according to claim 37, wherein the second co-reactant gas comprises an oxygen:hydrogen gas mixture.
40. (Original) The method of claim 39, wherein the oxygen:hydrogen gas mixture has a mole ratio in a range of about 1:1 to about 1:3.
41. (Previously Presented) The method of claim 13, wherein the first and the second ruthenium precursors are the same.
42. (Cancelled)
43. (Previously Presented) The method according to claim 13, wherein the first and the second ruthenium precursors are different,
44. (Cancelled)
45. (Previously Presented) The method of claim 43, wherein the first ruthenium precursor is selected from the group consisting of ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, and ruthenium oxides and second ruthenium precursor is selected from the group consisting of ruthenocenes, ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, ruthenium oxides and ruthenium halides.
46. (Previously Presented) The method of claim 43, wherein the first ruthenium precursor is a ruthenium β -diketonate and the second ruthenium precursor is a ruthenocene.
47. (Previously Presented) The method of claim 1, wherein the rate of introduction of the second ruthenium precursor is in a range of about 5 $\mu\text{mol}/\text{min}$ to about 20 $\mu\text{mol}/\text{min}$.

2771-696

48. (Original) The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 8 $\mu\Omega$ -cm to about 25 $\mu\Omega$ -cm, and has a thickness in a range of from about 10.0 nm to about 35.0 nm thick.
49. (Original) The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 12 $\mu\Omega$ -cm to about 25 $\mu\Omega$ -cm, and has a thickness in a range of from about 5.0 nm to about 15.0 nm thick.
50. (Original) The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 20 $\mu\Omega$ -cm to about 125 $\mu\Omega$ -cm, and has a thickness in a range of from about 2.0 nm to about 5.0 nm thick.
51. (Original) The method of claim 1, wherein the resistivity of the ruthenium thin film is in a range of about 10 $\mu\Omega$ -cm to about 100 $\mu\Omega$ -cm.
52. (Original) The method of claim 1, wherein the thickness of the ruthenium thin film is in a range of about 25 Å to about 350 Å.
53. (Original) The method of claim 1, wherein the rate of deposition of the upper layer is in a range of about 5 Å/min to about 1 Å/min.
54. (Previously Presented) The method of claim 1, wherein the source of either or both ruthenium precursors in the respective gas mixture is a solid and is delivered to the chemical vapor deposition chamber by a solid delivery approach.
55. (Original) The method of claim 54, further comprising the separate addition of a solvent to the solid delivery approach.
56. (Previously Presented) The method of claim 1, wherein the source of either or both ruthenium precursors in the respective gas mixture is a liquid or a solution and is delivered by a liquid delivery approach.
57. (Previously Presented) The method of claim 1, further comprising the step of annealing the nucleation layer prior to deposition of the upper layer.
58. (Previously Presented) The method of claim 1, wherein from about 80 mole% to about 90 mole% of the first ruthenium precursor/co-reactant gas mixture is oxygen.
59. (Previously Presented) The method of claim 1, wherein from about 80 mole % to about 95 mole % of the first ruthenium precursor/co-reactant gas mixture is oxygen and from about 1 mole % to about 20 mole % of the second ruthenium precursor/co-reactant gas mixture is oxygen.

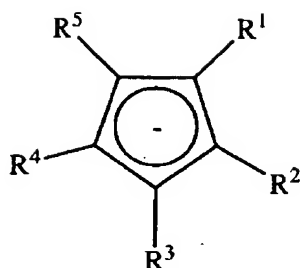
2771-696

60. (Original) The method of claim 1, wherein the ruthenium thin film has an impurity content of less than about 2 atomic%.
61. (Original) The method of claim 1, wherein the substrate comprises a metallic portion and a dielectric portion.
62. (Original) The method of claim 61, wherein the nucleation layer on the metallic and dielectric portions of the substrate is a peel-resistant layer film.
63. (Previously Presented) The method of claim 59 wherein the second co-reactant gas is a mixture of oxygen and hydrogen.
64. (Previously Presented) The method of claim 1, wherein each co-reactant gas is individually selected from the group consisting of oxygen, hydrogen, steam, nitrous oxide, ozone, carbon monoxide, carbon dioxide, and mixtures of oxygen and hydrogen.
65. (Currently Amended) A method for depositing a ruthenium thin film onto a substrate, said method comprising:
- (a) depositing a nucleation layer comprising ruthenium onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited from a nucleation layer ruthenium precursor/co-reactant gas mixture, the mixture having comprising at least a 30 mole % oxygen content, of a co-reactant gas in an oxidizing environment under nucleation layer CVD conditions;
 - (b) deoxygenating the so formed nucleation layer in a reducing environment, in the absence of the ruthenium precursor/co-reactant gas mixture; and
 - (c) sequentially repeating steps (a) and (b) until the ruthenium thin film of desired thickness is deposited onto the substrate.
66. (Original) The method of claim 65, wherein said deoxygenating comprises exposing said nucleation layer to a gas mixture comprising a reducing agent and optionally, an inert gas.
67. (Original) The method of claim 66, wherein the reducing agent comprises hydrogen.
68. (Previously Presented) The method of claim 65, wherein the deoxygenating step is conducted under conditions comprising pressure in a range of about 0.1 Torr to about 100 Torr and temperature in a range of about 250°C to about 350°C.
69. (Previously Presented) The method of claim 65, wherein the co-reactant gas is oxygen.

2771-696

70. (Previously Presented) The method of claim 65, wherein the temporal length of the deposition of the initial nucleation layer is greater than that of the succeeding deposition steps.
71. (Previously Presented) The method of claim 65, wherein the deposited nucleation layer comprises ruthenium oxide.
72. (Original) The method of claim 65, wherein the nucleation layer CVD conditions comprise temperature in a range of about 250°C and about 340°C.
73. (Original) The method of claim 65, wherein the nucleation layer CVD conditions comprise pressure in a range of about 0.1 Torr and about 8 Torr.
74. (Previously Presented) The method of claim 65, wherein the ruthenium precursor/co-reactant gas mixture further comprises an inert gas.
75. (Previously Presented) The method of claim 65, wherein the deoxygenation is accomplished by annealing.
76. (Previously Presented) The method of claim 65, wherein the flow rate of the ruthenium precursor is sufficient to maintain surface reaction rate-limited deposition.
77. (Previously Presented) The method of claim 65, wherein the CVD conditions include a pressure of from about 0.1 Torr to about 5.0 Torr, a temperature of from about 250°C and about 340°C, and a flow rate of the ruthenium precursor of from about 15 $\mu\text{mol/min}$ to about 30 $\mu\text{mol/min}$ and the co-reactant gas is oxygen and is present in a concentration of from about 80 mole % to about 95 mole %.
78. (Previously Presented) The method of claim 77, wherein the co-reactant gas is present in a concentration of from about 80 mole % to about 90 mole %.
79. (Cancelled)
80. (Previously Presented) The method of claim 65, wherein the co-reactant gas comprises from about 80 mole% to about 95 mole% of the ruthenium precursor/co-reactant gas mixture.
81. (Previously Presented) The method of claim 80, wherein the co-reactant gas comprises oxygen.
82. (Previously Presented) The method of claim 65, wherein the ruthenium precursor comprises a ruthenium compound selected from the group consisting of ruthenocenes, ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, ruthenium oxides and ruthenium halides.
83. (Original) The method according to claim 82, wherein the ruthenocenes have the formula $(\text{Cp}')\text{Ru}(\text{Cp}'')$, where Cp' and Cp'' can be same or different and have the general formula:

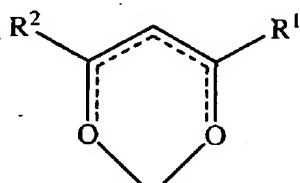
2771-696



where R¹ - R⁵ are independently selected from the group consisting of H, F, and straight-chained or branched C₁ - C₅ alkyl groups.

84. (Original) The method according to claim 82, wherein the ruthenocene comprises Ru(EtCp)₂ or Ru(Cp)₂,

85. (Original) The method according to claim 82, wherein the ruthenium β-diketonates have the formula Ru(β-diketonate)₃, where β-diketonate has the general formula:



where R¹ and R² are independently selected from the group consisting of H, F, straight-chained or branched C₁ - C₅ alkyl groups, and fluorine-substituted straight-chained or branched C₁ - C₅ alkyl groups.

86. (Original) The method of claim 82, wherein the ruthenium β-diketonate comprises a compound selected from the group consisting of: tris(2,4-pentanedionate) ruthenium (Ru(acac)₃); tris(1,1,1-trifluoro-2,4-pentanedionate) ruthenium (Ru(tfac)₃); tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ruthenium (Ru(thd)₃); tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) ruthenium (Ru(hfac)₃); tris(2,2,7-tetramethyl-3,5-octanedionato) ruthenium (Ru(tod)₃); tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) ruthenium (Ru(fod)₃); and tris(2,4-octanedionato) ruthenium (Ru(od)₃).

87. (Original) The method of claim 82, wherein the ruthenium β-diketonate comprises Ru(thd)₃ or Ru(hfac)₃.

2771-696

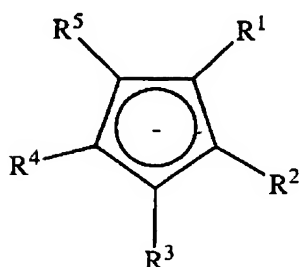
88. (Previously Presented) The method of claim 65, wherein the rate of introduction of the ruthenium precursor is in a range of about 15 $\mu\text{mol}/\text{min}$ to about 30 $\mu\text{mol}/\text{min}$.
89. (Previously Presented) The method of claim 65, wherein the substrate comprises a substrate material selected from the group consisting of silicon, silicon dioxide, silicon nitride, hafnium silicon oxide, hafnium silicon oxynitride, Co(WP), copper, titanium nitride, titanium aluminum nitride, tantalum nitride, tantalum pentaoxide, barium strontium titanate and lead zirconate titanate.
90. (Original) The method of claim 65, wherein the resistivity of the nucleation layer is less than about 250 $\mu\Omega\text{-cm}$.
91. (Original) The method of claim 65, wherein the rate of deposition of the nucleation layer is in a range of about 5 $\text{\AA}/\text{min}$ to about 1 $\text{\AA}/\text{min}$.
92. (Original) The method of claim 65, wherein the resistivity of the ruthenium thin film is in a range of about 15 $\mu\Omega\text{-cm}$ to about 50 $\mu\Omega\text{-cm}$, and has a thickness in a range of from about 3.0 nm to about 10.0 nm.
93. (Original) The method of claim 65, wherein the resistivity of the ruthenium thin film is in a range of about 15 $\mu\Omega\text{-cm}$ to about 30 $\mu\Omega\text{-cm}$, and has a thickness in a range of from about 4.0 nm to about 8.0 nm.
- 94-96. (Cancelled)
97. (Previously Presented) A method for depositing a ruthenium thin film onto a substrate, said method comprising:
- (a) depositing a nucleation layer comprising ruthenium onto the substrate by chemical vapor deposition, wherein the nucleation layer is deposited using a nucleation layer mixture containing a first ruthenium precursor under nucleation layer CVD conditions; and
 - (b) depositing an upper layer comprising ruthenium onto the nucleation layer by chemical vapor deposition, wherein the upper layer is deposited using an upper layer mixture containing a second ruthenium precursor, different from the first, under upper layer CVD conditions.
98. (Previously Presented) The method of claim 97, wherein the first and second ruthenium precursors are selected from the group consisting of ruthenocenes, ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, ruthenium oxides and ruthenium halides.

2771-696

99. (Previously Presented) The method of claim 97, wherein the first ruthenium precursor is selected from the group consisting of ruthenium β -diketonates, fluorinated ruthenium β -diketonates, ruthenium carbonyls, and ruthenium oxides.

100. (Previously Presented) The method of claim 97, wherein the first ruthenium precursor is a ruthenium β -diketonate and the second ruthenium precursor is a ruthenocene.

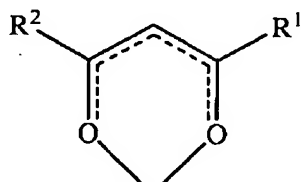
101. (Previously Presented) The method of claim 100, wherein the ruthenocene has the formula $(Cp')Ru(Cp'')$, where Cp' and Cp'' can be same or different and have the general formula:



where $R^1 - R^5$ are independently selected from the group consisting of H, F, and straight-chained or branched $C_1 - C_5$ alkyl groups.

102. (Previously Presented) The method of claim 100, wherein the ruthenocene comprises $Ru(EtCp)_2$ or $Ru(Cp)_2$.

103. (Previously Presented) The method of claim 100, wherein the ruthenium β -diketonate has the formula $Ru(\beta\text{-diketonate})_3$, where β -diketonate has the general formula:



where R^1 and R^2 are independently selected from the group consisting of H, F, straight-chained or branched $C_1 - C_5$ alkyl groups, and fluorine-substituted straight-chained or branched $C_1 - C_5$ alkyl groups.

2771-696

104. (Previously Presented) The method of claim 100, wherein the ruthenium β -diketonate comprises a compound selected from the group consisting of: tris(2,4-pentanedionate) ruthenium ($\text{Ru}(\text{acac})_3$); tris(1,1,1-trifluoro-2,4-pentanedionate) ruthenium ($\text{Ru}(\text{tfac})_3$); tris(2,2,6,6-tetramethyl-3,5-heptanedionate) ruthenium ($\text{Ru}(\text{thd})_3$); tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) ruthenium ($\text{Ru}(\text{hfac})_3$); tris(2,2,7-tetramethyl-3,5-octanedionato) ruthenium ($\text{Ru}(\text{tod})_3$); tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) ruthenium ($\text{Ru}(\text{fod})_3$); and tris(2,4-octanedionato) ruthenium ($\text{Ru}(\text{od})_3$).
105. (Previously Presented) The method of claim 100, wherein the ruthenium β -diketonate comprises $\text{Ru}(\text{thd})_3$ or $\text{Ru}(\text{hfac})_3$.
106. (Previously Presented) The method of claim 97 wherein the deposited nucleation layer comprises ruthenium metal.
107. (Previously Presented) The method of claim 97, wherein the nucleation layer CVD conditions include a temperature of from about 250°C to about 340°C and a flow rate of the first ruthenium precursor of from about 15 $\mu\text{mol}/\text{min}$ to about 30 $\mu\text{mol}/\text{min}$ and the co-reactant gas is oxygen and is present in a concentration of from about 80 mole % to about 95 mole % and the upper layer CVD conditions include a temperature of from about 250°C to and about 400°C and a flow rate of the second ruthenium precursor of from about 5 $\mu\text{mol}/\text{min}$ to about 20 $\mu\text{mol}/\text{min}$ and from about 1 mole % to about 10 mole % of the second ruthenium precursor/co-reactant gas mixture comprises oxygen.
108. (Currently amended) The method of ~~the~~ claim 107, wherein the second co-reactant gas comprises an oxygen:hydrogen gas mixture.
109. (Currently amended) The method of claim 108, wherein the ~~more~~ ratio of oxygen to hydrogen is from about 1:1 to about 1:3.
110. (Previously Presented) The method of claim 97 wherein the flow of the first ruthenium precursor is sufficient to maintain a surface reaction rate-limited deposition and the flow of the second ruthenium precursor is less than that needed to maintain a surface reaction rate-limited deposition.
111. (Previously Presented) The method of claim 110, wherein the nucleation layer CVD conditions include a temperature of from about 250°C to about 340°C and the first co-reactant gas comprises more than 30mole % of the first ruthenium precursor/co-reactant gas mixture.
112. (Previously Presented) The method of claim 97, wherein the upper layer CVD conditions are more reducing than the nucleation layer CVD conditions.